

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C22B 3/00, B01J 45/00		A1	(11) International Publication Number: WO 91/17274 (43) International Publication Date: 14 November 1991 (14.11.91)
(21) International Application Number: PCT/BE91/00027			(74) Agent: SAELEMAEKERS, Juul; MHO-S.A. ACEC-UNION MINIERE N.V., Adolf Greinerstraat 14, B-2660 Hoboken (BE).
(22) International Filing Date:	3 April 1991 (03.04.91)		
(30) Priority data: 9000459	27 April 1990 (27.04.90)	BE	
(71) Applicant (for all designated States except US): S.A. ACEC-UNION MINIERE N.V. [BE/BE]; Avenue Emile-Rousseau, B-6001 Marcinelle (BE).			(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.
(72) Inventors; and (75) Inventors/Applicants (for US only): HAESEBROEK, Guy, Gustave, L., B. [BE/BE]; Floris Decuijperstraat 12, B-2640 Mortsel (BE). DE SCHEPPER, Achille, Josee, M. [BE/BE]; Esdoornlaan 8, B-2460 Lichtaart (BE).			Published <i>With international search report.</i>

(54) Title: METAL EXTRACTION BY ION EXCHANGE

(57) Abstract

Process for extracting Ge, Ga, In, As, Sb, Bi, Pt, Pd, Ni, and/or Co from an acid aqueous solution, wherein use is made of a resin with 8-hydroxyquinoline groups, resulting from the reaction of an aminated resin with an aldehyde and 8-hydroxyquinoline, characterized in that the aminated resin itself is obtained by imidoalkylation of a cross-linked styrene-copolymer and an ester or an ether of an N-hydroxyalkylimide and by hydrolysis of the imidoalkylation product.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

METAL EXTRACTION BY ION EXCHANGE

The present invention relates to a process for extracting one or more metals selected from the group consisting of Ge, Ga, In, As, Sb, Bi, Pt, Pd, Ni and Co from an acid aqueous solution containing said one or more metals, according to which the acid aqueous solution is contacted with a solid ion exchanger at a pH at which the ion exchanger absorbs said one or more metals, said ion-exchanger resulting from the reaction of a carrier material, containing NH- and/or NH₂-groups that are able to react with aldehydes, with

5 (a) an aldehyde and

10 (b) 8-hydroxyquinoline and/or an 8-hydroxyquinoline derivative, and possibly

15 (c) a swelling agent and/or a solvent.

Such a process is described in SU-A-407922. In this known process indium is extracted from sulfuric acid solutions of pH 1.05 and 2.9 by contacting the solutions with an ion exchanger resulting from the reaction of crosslinked polymers having primary or secondary aminogroups with formaldehyde and 8-hydroxyquinoline in water or alcohol, the aminated crosslinked polymers themselves resulting from either the condensation of amines with epichlorohydrin or the amination of chloromethylated styrene-divinylbenzene-copolymers.

The aim of the present invention is to provide a process such as defined herebefore, which gives better extraction results than the prior art process.

Therefore, according to the invention use is made of an ion exchanger resulting from the said reaction, when the carrier material is one that is obtainable by amidoalkylation, preferably by imidoalkylation with an ester or an ether of a N-hydroxyalkylimide, of a crosslinked styrene-copolymer and by subsequent hydrolysis of the amido- or imidoalkylation product.

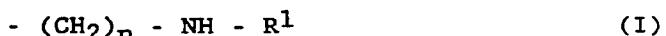
Preferred modes of carrying out the process of the invention are described in the hereto attached claims 2-29.

35 The process of the invention is particularly useful for extracting Ge, Ga and/or In from ZnSO₄ solutions used in the electrowinning of zinc, for separating As, Bi and Sb impurities from sulfuric

acid solutions and for separating Pt or Pd impurities from AgNO_3 solutions used in the electrorefining of silver.

As to the preparation of the ion exchanger used in the process of the present invention, the following should be noted.

5 The carrier material contains preferably at least one reactive group of the general formula



10 wherein

R^1 = H or a possibly substituted and possibly unsaturated alkyl-, cycloalkyl- or alicyclic rest with 1 to 10 C-atoms - preferably methyl - or a possibly substituted aromatic rest with 6 to 10 C-atoms and

15 $n = 1$ or 2.

Carrier materials, wherein $\text{R}^1 = \text{H}$ and $n = 1$, are especially preferred. A macroporous aminomethylated styrene-divinylbenzene-copolymer is used as a preferred carrier material.

20 The carrier material can be prepared by a Friedel-Crafts reaction of a crosslinked, water-insoluble organic polymer containing aromatic nuclei, with an imidoalkylation agent in the presence of a swelling agent for the polymer and of an acid catalyst and by subsequent hydrolysis of the imidoalkylated polymer in accordance with DE-PS 2161628 and DE-PS 2418976.

25 The esters of N-hydroxyalkylimides with lower aliphatic carboxylic acids (DE-PS 2418976) as well as bis-(dicarbonimidooalkyl)-ethers (DE-PS 2161628) can be used as imidoalkylation agents.

30 As N-hydroxyalkylimides which can be used there should be mentioned the di-methylimides and di-ethylimides of aliphatic $\text{C}_4\text{-C}_6$ dicarboxylic acids and of aromatic o-dicarboxylic acids. The N-hydroxymethylimides are preferably used.

35 The crosslinked, water-insoluble organic polymers containing aromatic nuclei is preferably an aromatic vinyl compound of the type obtained by the copolymerisation of monovinyl and polyvinyl compounds. Such copolymers are known per se and are obtained by known methods. The copolymer may be either microporous, i.e. has a gel

structure, or macroporous.

Preferred copolymers are those which consist of a major amount of aromatic monovinylcompounds and of a minor amount of aromatic or aliphatic polyvinyl compounds.

5 Suitable swelling agents for the polymer are, above all, halogenated hydrocarbons or polar organic solvents such as nitro compounds.

Suitable catalysts include the usual Friedel-Crafts catalysts, such as AlCl_3 or FeCl_3 and, especially, sulphuric acid.

10 The reaction of the organic polymer with the ester of the N-hydroxyalkylimide is carried out at temperatures of 0-150°C. The ester is used in such quantities that there are from 0.5 to 4 mols of ester per mol of aromatic nuclei in the polymer. The catalyst is generally used in quantities ranging from 0.1 to 1.5 mol per mol of 15 ester.

15 The reaction can be carried out by initially preparing the ester of the N-hydroxyalkylimide in the swelling agent and swelling the polymer in this solution, whereafter the acid catalyst is added and the mixture is brought to the reaction temperature. On completion of the acylimidoalkylation reaction the acyl radical is split off from the reaction products in a known manner, by subjecting the acylimidoalkylation product to alkaline or acid hydrolysis.

20 Preferred carrier materials are aminomethyl-polystyrene-divinylbenzene resins with a nitrogen content of 8-12 wt. % in the dry material and with a degree of crosslinking of 2-12 %, preferably 4-8 %, and useful capacities of 1.5-3.5 equivalent/l, preferably 2.5-3 equivalent/l, in accordance with DE-PS 2418976.

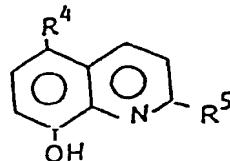
25 The aldehydes, which can be used for preparing the ion exchanger that is used in the process of the present invention, are those 30 which are suited to undergo the Mannich-reaction with the amino-groups of the carrier material and 8-hydroxyquinolines according to formula III.

These are aldehydes of the general formula :

in which R³ stands for hydrogen, an alkylrest with 1-4, especially 1-2 C-atoms or a possibly substituted aromatic hydrocarbon rest with 6-10 C-atoms, such as propionaldehyde, butyraldehyde, iso-butyraldehyde, especially formaldehyde, acetaldehyde and benzaldehyde.

5 The 8-hydroxyquinolines, which can be used for preparing the ion exchanger used in the process of the present invention, are those of the general formula III

10



(III)

in which R⁴ = H or a halogen atom or -SO₃H and R⁵ = H or CH₃.

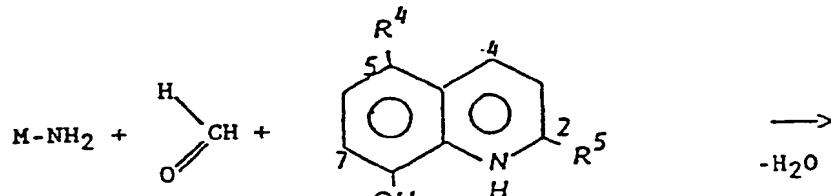
15 Very suitable compounds are those wherein R⁴ = H or chlorine and R⁵ = H.

20 The synthesis of the ion exchanger is normally carried out in the presence of a swelling agent and/or a solvent. Suitable swelling agents and/or solvents are water, to which acids and bases may be added, as well as C₁-C₄-alcohols, especially methanol and ethanol.

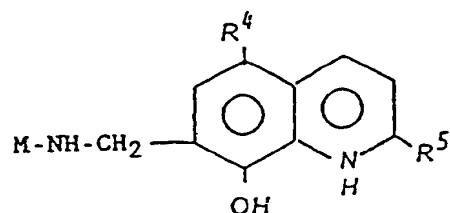
25 The synthesis itself consists in reacting the carrier materials (M) with aldehydes and 8-hydroxyquinolines by a Mannich reaction :

25

30



35



The synthesis is carried out in the reaction conditions which are well known for carrying out Mannich-reactions. The aminomethylation of 8-hydroxyquinolines of formula III then occurs almost selectively at the 7-position.

5 Preferably, the carrier material is allowed to swell in a solvent or a solvent mixture before the reaction.

The reaction temperature can lie, dependent on the nature of the components, between 20-100°C, preferably between 20-80°C and particularly between 50-70°C. The reaction time can amount up to 10 48 h; as a rule, however, it lies between 5 and 24 h.

The molar ratio aldehyde : 8-hydroxyquinoline can vary between 2:1 and 1:1, but is preferably about 1-1.5:1. The quantities of aldehyde and 8-hydroxyquinoline depend on the reactive aminogroups that are accessible on the carrier material. They are preferably 15 used in such quantities that all accessible aminogroups undergo the Mannich-reaction. In most cases, a ratio aminogroups : 8-hydroxyquinoline of 1:1 to 1:1.5 will be sufficient.

On completion of the reaction the resin is separated, washed with water, possibly in the presence of bases or acids, and/or solvents. The resin, which is so freed from not converted soluble 20 reaction components, can be used directly for the extraction process.

Examples of the preparation of ion exchangers that can be used in the process of the present invention :

25

4 different aminomethylated styrene-divinylbenzene resins (I, II, III and IV), to be used as carrier materials, were prepared in accordance with DE-PS 2418976, example 2, such as described hereunder for resin I :

30

354 g of N-hydroxymethylphthalimide, dissolved in 1100 g of dichloroethane, are heated for 5 hours to reflux temperature with 227 g of acetic acid anhydride. 150 g of resin beads made of a macroporous styrene polymer crosslinked with 6 % divinylbenzene are swollen in this ester solution for 1 hour at 60°C. 240 g of concentrated sulphuric acid are then added dropwise over a period of 1 hour at reflux temperature and the reaction mixture is then stirred at the

same temperature for 20 hours. After the reaction product has been separated off, it is suspended in 1000 ml of a 10 % aqueous ammonia solution. The residues of dichloroethane are removed from this suspension by azeotropic distillation. The reaction product is then 5 separated off and hydrolyzed by heating for 10 hours at 180°C with a 40 % sodium hydroxyde solution in an autoclave. After filtration and washing the aminomethyl-polystyrene-divinylbenzene resin I is obtained.

10 The properties of resin I are given in Table 1.
Resins II, III and IV (see Table 1) were prepared in an analogous way.

Table 1

15	Resin	N-content* in dry material %	Degree of crosslinking %	Capacity** equi- valent/l	Type of resin
20	I	11.1	6	3.0	macroporous
	II	8.9	8	2.6	macroporous
	III	8.8	5	2.4	macroporous
	IV	9.1	4	2.8	gel structure

*) according to elementary analysis

25 **) the data relate to the moist resins (see DIN 54402, DIN 54408, DIN 54400)

(1) 314 g of the moist aminomethyl-polystyrene-divinylbenzene resin 30 I (corresponding to 100 g of dry material), 165 g of 8-hydroxy-quinoline and 470 ml of methanol are stirred for 1.5 hour at 60°C. 50.5 g of p-formaldehyde are then added and the stirring is continued for 5 hours at 60°C. The resin is filtered off. In order to remove not converted reaction components the resin 35 is washed successively with 300 ml of respectively methanol, water, 4N H₂SO₄, water, 1.5 N NaOH and finally with water till the effluent is neutral.

The yield of moist resin is 350.6 g, corresponding to 201 g of dry material. The calculated 8-hydroxyquinoline content is 3.2 mol per kg dry resin (see table 2, resin A).

The water content is 42.7 %.

5 (2) The conversion of resin I such as described in example (1) is repeated with different reagent ratios, solvents and reaction times, whereby obtaining the resins Aa-Ad (see table 2).

Table 2

	Resin	A	Aa	Ab	Ac	Ad
10	g 8-hydroxyquinoline	165	165	165	96	165
15	g p-formaldehyde	50.5	50.5	37	20	50.5
	Solvent	CH ₃ OH	CH ₃ OH	CH ₃ OH	CH ₃ OH	C ₂ H ₅ OH
	Reaction time h	5	24	24	5	5
20	Yield of dry material in g	201	214	192	155	186
	Water content of the resin %	42.7	38.6	44.2	48.3	42.8
	Wt. per liter in g/ml*	0.81	0.81	0.80	0.79	0.80
	Content Mol 8-hydroxyquinoline kg dry material	3.2	3.4	3.1	2.3	3.0

*) in accordance with DIN 54408

25 (3) Resins II, III and IV are converted in the same way as described in example (1) for resin I, whereby obtaining the resins B, C and D (see Table 3).

Resins A, Aa, Ab, Ac, Ad, B, C and D are thus representative of 30 the ion exchangers which can be used in the process of the present invention.

An ion exchanger to be used in the above discussed prior art process was prepared starting from a commercially available amination product of chloromethylated macroporous polystyrene-divinylbenzene resin with a nitrogen content of 6.3 %. This aminated resin was subjected to the Mannich-reaction as described in example (1), whereby obtaining ion exchanger E (see Table 3).

Table 3

5	Resin	To be used in the process of the invention				To be used in the prior art process
		A	B	C	D	
Starting resin	I	II	III	IV	Commercial macroporous aminomethyl-polystyrene -divinylbenzene	
g 8-hydroxyquinoline	165	165	165	165	160	
g formaldehyde	50.5	50.5	50.5	50.5	33	
Solvent	CH ₃ OH	CH ₃ OH	CH ₃ OH	CH ₃ OH	C ₂ H ₅ OH	
Reaction time h	5	5	3	3	40	
Yield of dry material in g	201	147	171	213	131	
Water content of the resin %	42.7	46.4	38.3	30	58.3	
Wt. per liter in g/ml*	0.81	0.77	0.78	0.87	0.75	
Content <u>Mol 8-hydroxyquinoline</u> kg dry material	3.2	2.0	2.6	3.4	1.5	

*) in accordance with DIN 54408

20 The process of the invention is illustrated by the following examples.

Example 1

25 The extraction of Ge, Ga, In, Sb, Bi, Pt, Pd, Ni and Co from acid solutions is carried out by one of the following methods :

Method a :

30 A quantity of moist resin corresponding to 5 g of dry material is contacted for 3 minutes with 4 N H₂SO₄, then filtered off and washed until neutral with 2 l of water. The resin is finally washed with solution 1 (see Table 4) and then stirred for 24 h in 110 ml of a solution of the metal (6 g/l of metal ions in solution 1). The metal content of the solution is determined before and after 35 contact of the solution with the resin, by titration or by atomic absorption spectroscopy. Using these data, the metal loading of the resin in g Mⁿ⁺/l resin is calculated.

When the quantity of metal used in method a is not sufficient for saturating the resin with metal, then method b is used.

Method b :

5

One operates in the same way as in method a, but instead of using 110 ml of metal solution one uses 220 ml.

For the extraction of expensive metals one uses method c.

10

Method c :

One operates in the same way as in method a, but one uses a limited quantity of moist resin corresponding to 0.2 g of dry material and a 15 solution of 1 m equivalent of metal in 50 ml of solution 1.

The results are given in Tables 4 and 4a.

Table 4

20

Metal	Sb ^{3/5+}	Bi ³⁺	Ge ⁴⁺	Ga ³⁺	In ³⁺	Pd ²⁺	Pt ⁴⁺	Co ²⁺ (1)	Co ²⁺ (2)	Ni ²⁺ (1)	Ni ²⁺ (2)
Solution 1	HCl	HNO ₃	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄	HCl	HCl	H ₂ SO ₄			
pH	0.4	0.3	3	2.5	3	1.2	0.0	2	5	2	5
Method	b	b	a	a	c	c	c	a	a	a	a

25

Table 4a

30

Metal	Sb ^{3/5+}	Bi ³⁺	Ge ⁴⁺	Ga ³⁺	In ³⁺	Pd ²⁺	Pt ⁴⁺	Co ²⁺ (1)	Co ²⁺ (2)	Ni ²⁺ (1)	Ni ²⁺ (2)
Resin	Metal loading in g metal/l										
A	113.8	123.8	44.6	46.1	58.3	133.9	131	14.4	37	17.3	38.9
B	95.1	95.9	33.2	35.3	47.6	109.1	107	-	-	-	-
C	107.5	121.9	43.7	-	-	119.0	-	-	-	-	-
D	72.0	0	53.7	-	-	13.4	-	-	-	-	-
E (prior art process resin)	41.5	39.7	13.0	13.6	19.5	38.4	40.0	3.4	-	13	-

35

10

Example 2

The re-extraction of some metals from resin A is carried out as follows :

5

Resin A resulting from example 1 is poured into a column and washed with 200 ml of solution 1. The washwater is rejected. The resin is then treated with 500 ml of solution 2 (re-extraction). The metal content of the obtained eluate is determined.

10 The re-extraction yield (in %) is calculated as follows :
(g of re-extracted metal : g of fixed metal) x 100.

The operation is carried out in downflow at a rate of 2-4 bed volumes per hour.

15

The results are given in Table 5.

Table 5

20

Metal	Solution 1	Solution 2	Re-extraction yield %
Co ²⁺	pH 5	2M H ₂ SO ₄	62.4
Ni ²⁺	pH 5	2M H ₂ SO ₄	80.8
Sb ^{3+/5+}	1.5 M HCl	4M NaOH	42.7
Bi ³⁺	pH 0.3	5M H ₂ SO ₄	97
Ga ³⁺	pH 2.5	2M H ₂ SO ₄	88.6
In ³⁺	pH 3	2M H ₂ SO ₄	100
Ge ⁴⁺	pH 3.5	3M KOH	91
Pd ²⁺	0.1M HCl	8M HCl	84.5

Claims

1. Process for extracting one or more metals selected from the group consisting of Ge, Ga, In, As, Sb, Bi, Pt, Pd, Ni and Co from an acid aqueous solution containing said one or more metals, according to which the acid aqueous solution is contacted with a solid ion exchanger at a pH at which the ion exchanger absorbs said one or more metals, said ion exchanger resulting from the reaction of a carrier material, containing NH₂- and/or NH₃⁺-groups that are able to react with aldehydes, with
 - (a) an aldehyde and
 - (b) 8-hydroxyquinoline and/or an 8-hydroxyquinoline derivative, and possibly
 - (c) a swelling agent and/or a solvent,
- 15 characterized in that one uses an ion exchanger resulting from the said reaction, when the carrier material is one that is obtainable by amidoalkylation, preferably by imidoalkylation with an ester or an ether of a N-hydroxyalkylimide, of a crosslinked styrene-copolymer and by subsequent hydrolysis of the amido- or imidoalkylation product.
- 20 2. Process according to claim 1, characterized in that said one metal is Ge and the pH is below 5, preferably below 2.
3. Process according to claim 2, characterized in that Ge is eluted from the ion exchanger by an aqueous solution of NaOH with a normality of at least 0.1, preferably 0.5-5.
- 25 4. Process according to claim 1, characterized in that said one metal is Ga and the pH is 0.5-5, preferably 1-3.
5. Process according to claim 4, characterized in that Ga is eluted from the ion exchanger either by an aqueous solution of NaOH with a normality of at least 0.25, preferably 0.5-5, or by an aqueous solution of H₂SO₄ or HCl with a normality of at least 0.5, preferably 1-5.
- 30 6. Process according to claim 1, characterized in that said one metal is In and the pH is 0.5-4, preferably 1-3.
- 35 7. Process according to claim 6, characterized in that In is eluted from the ion exchanger by an aqueous solution of H₂SO₄ or HCl with a normality of at least 0.5, preferably 1-5.

8. Process according to claim 1, characterized in that said more metals are Ge and Ga and the pH is 0.5-3, preferably 1-2.
9. Process according to claim 8, characterized in that Ge and Ga are eluted from the ion exchanger by an aqueous solution of NaOH with a 5 normality of at least 0.25, preferably 0.5-5.
10. Process according to claim 8, characterized in that Ga is eluted from the ion exchanger by an aqueous solution of H_2SO_4 or HCl with a normality of at least 0.5, preferably 1-5, and then Ge is eluted by an aqueous solution of NaOH with a normality of at least 0.1, 10 preferably 0.5-5.
11. Process according to claim 1, characterized in that said more metals are Ge and In and the pH is 0.5-3, preferably 1-2.
12. Process according to claim 11, characterized in that In is eluted from the ion exchanger by an aqueous solution of H_2SO_4 or HCl 15 with a normality of at least 0.5, preferably 1-5, and Ge is eluted by an aqueous solution of NaOH with a normality of at least 0.1, preferably 1-5.
13. Process according to claim 1, characterized in that said more metals are Ga and In and the pH is 0.5-4, preferably 1-3.
- 20 14. Process according to claim 13, characterized in that Ga and In are eluted from the ion exchanger by an aqueous solution of H_2SO_4 or HCl with a normality of at least 0.5, preferably 1-5.
15. Process according to claim 13, characterized in that Ga is eluted from the ion exchanger by an aqueous solution of NaOH with a 25 normality of at least 0.25, preferably 1-5, and then In is eluted by an aqueous solution of H_2SO_4 or HCl with a normality of at least 0.5, preferably 1-5.
16. Process according to claim 1, characterized in that said more metals are Ge, Ga and In and the pH is 0.5-2.5, preferably 1-1.5.
- 30 17. Process according to claim 16, characterized in that Ge and Ga are eluted from the ion exchanger by an aqueous solution of NaOH with a normality of at least 0.25, preferably 1-5, and then In is eluted with an aqueous solution of H_2SO_4 or HCl with a normality of at least 0.5, preferably 1-5.
- 35 18. Process according to claim 16, characterized in that Ga and In are eluted from the ion exchanger by an aqueous solution of H_2SO_4 or

HCl with a normality of at least 0.5, preferably 1-5, and then Ge is eluted with an aqueous solution of NaOH with a normality of at least 0.1, preferably 1-5.

19. Process according to any of claims 2-18, characterized in that 5 the solution, from which the metal or metals are extracted, is a zinc sulfate solution.

20. Process according to claim 1, characterized in that said one metal is Sb and the pH is below 1, preferably below 0.5.

21. Process according to claim 20, characterized in that Sb is 10 eluted from the ion exchanger by an aqueous solution of KOH with a normality of at least 0.1, preferably 0.5-3.

22. Process according to claim 1, characterized in that said more metals are As, Bi and Sb, said acid aqueous solution being a 15 solution of H₂SO₄ with a normality of 1-5, preferably 3-5, and said pH being the pH of said acid aqueous solution.

23. Process according to claim 22, characterized in that said As, Bi and Sb are eluted from the ion exchanger with an aqueous solution of HCl having a pH below 1.

24. Process according to claim 22, characterized in that As and Sb 20 are eluted from the ion exchanger by an aqueous solution of KOH with a normality of at least 0.1, preferably 0.5-3, and then Bi is eluted with an aqueous solution of HCl having a pH below 1.

25. Process according to claim 22, 23 or 24, characterized in that the solution, from which As, Bi and Sb are extracted, is a copper sulfate solution.

26. Process according to claim 1, characterized in that said one or 30 more metals are Ni and/or Co and the pH is comprised between 1 and 7.

27. Process according to claim 26, characterized in that Ni and/or Co are eluted from the ion exchanger by an aqueous solution having a pH below 1.

28. Process according to claim 1, characterized in that said one or 35 more metals are Pt and/or Pd, said acid aqueous solution being a solution of HCl and/or HNO₃ with a normality of 0.01-4, preferably 0.5-3, and said pH being the pH of said acid aqueous solution.

29. Process according to claim 28, characterized in that Pt and/or Pd are eluted from the ion exchanger by either an aqueous solution of HCl with a normality higher than 4, or with an aqueous solution of NH₄OH with a normality higher than 0.1, preferably higher than 2, or with an aqueous solution of KSCN with a normality higher than 0.1, preferably higher than 1, or with an aqueous solution of thiourea with a thiourea content of more than 0.1 % by wt., preferably more than 3 %.

INTERNATIONAL SEARCH REPORT

International Application No PCT/BE 91/00027

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 22 B 3/00, B 01 J 45/00

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC ⁵	C 22 B, B 01 J

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4215219 (PATCHORNICK et al.) 29 July 1980 see claims 1-4 ---	1
A	US, A, 4085261 (PATCHORNICK et al.) 18 April 1978 see claims 1-5 ---	1
A	US, A, 4409189 (BORROWMAN et al.) 11 October 1983 ---	
A	US, A, 4180628 (MARCHANT et al.) 25 December 1979 ---	
A	EP, A, 0234319 (MITSUBISHI CHEMICAL INDUSTRIES) 2 September 1987 ---	
A	Patent Abstracts of Japan, volume 13, no.21 (C-560), 18 January 1989; & JP, A, 63224735 (HIROAKI EGAWA) 19 September, 1988 see the whole abstract ---	
A	US, A, 4631177 (YOTSUYAUAGI et al.) 23 December 1983 -----	

* Special categories of cited documents: ¹⁰
 "A" document defining the general state of the art which is not
 considered to be of particular relevance
 "E" earlier document but published on or after the international
 filing date
 "L" document which may throw doubts on priority claim(s) or
 which is cited to establish the publication date of another
 citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or
 other means
 "P" document published prior to the international filing date but
 later than the priority date claimed

"T" later document published after the international filing date
 or priority date and not in conflict with the application but
 cited to understand the principle or theory underlying the
 invention
 "X" document of particular relevance; the claimed invention
 cannot be considered novel or cannot be considered to
 involve an inventive step
 "Y" document of particular relevance; the claimed invention
 cannot be considered to involve an inventive step when the
 document is combined with one or more other such documents,
 such combination being obvious to a person skilled
 in the art
 "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

5th June 1991

Date of Mailing of this International Search Report

30.07.91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

miss T. MORTENSEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

BE 9100027
SA 45892

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 16/07/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 4215219	29-07-80	AU-A- CA-A- DE-A- GB-A- US-A-	7798775 1055034 2504397 1503571 4085261	12-08-76 22-05-79 14-08-75 15-03-78 18-04-78
US-A- 4085261	18-04-78	AU-A- CA-A- DE-A- GB-A- US-A-	7798775 1055034 2504397 1503571 4215219	12-08-76 22-05-79 14-08-75 15-03-78 29-07-80
US-A- 4409189	11-10-83	None		
US-A- 4180628	25-12-79	None		
EP-A- 0234319	02-09-87	AU-B- AU-A- JP-A- US-A-	594742 6808387 62275026 4865823	15-03-90 06-08-87 30-11-87 12-09-89
US-A- 4631177	23-12-86	JP-C- JP-A- JP-B-	1536043 60042234 63016333	21-12-89 06-03-85 08-04-88